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TITLE OF THE INVENTIONPreparation of biuret-containing polyisocyanates

The present invention relates to a process for the preparation of  
5 polyisocyanates which contain one or more biuret groups, by  
reacting

a) an aliphatic or cycloaliphatic polyisocyanate (isocyanate a)  
with

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b) a tertiary alcohol or a mixture of water and a tertiary  
alcohol (biuretizing agent b)

at from 100 to 250°C.

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Description of the Background

In the text below, the adjective "biuret-containing" indicates  
that the compounds it describes have a content of biuret groups.

The preparation of biuret-containing polyisocyanates is a  
20 reaction which has been described at some length (cf. H.J. Laas  
et al., J. prakt. Chem. 336 (1994) 185-200).

Numerous patents disclose, for example, the reaction of water  
with an excess of polyvalent isocyanates to give, first of all,  
25 urea groups, which undergo further reaction with the isocyanates  
to form biuret groups (cf. DE-A 1 101 394). The difficulty of  
preparing homogenous mixtures of water and the isocyanate means  
that in the course of this reaction, in practice, local excesses  
of water always result in the formation of greater or lesser  
30 proportions of insoluble polymeric urea-containing compounds  
which are deposited in the reaction vessel or in the off-gas  
space.

US-A 4 028 392 describes a process in which this problem is  
35 avoided by employing water in the form of an aqueous solution  
with a solvent which is inert to isocyanates. The disadvantage  
here is the need to separate the solvent from the product again  
by distillation.

SUMMARY OF THE INVENTION

40 These problems can be overcome using the process known from  
DE-A 1 543 178, in which a monohydric tertiary alcohol such as  
tert-butanol is used instead of water. The alcohol reacts at 70°C  
or more with an excess of isocyanate to form biuret-containing  
polyisocyanates and, as by-products, an olefin - isobutene for  
45 example - and CO<sub>2</sub>, which can be removed from the reaction mixture  
with ease.

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It is probable that the alcohol and the isocyanate react initially to form a urethane which decomposes into an amine, CO<sub>2</sub> and an olefin, and that the amine reacts with further isocyanate to give urea derivatives, and then to give biuret-containing  
5 polyisocyanates.

This reaction is preferably carried out in the presence of catalysts, with those recommended for this being acids such as strong inorganic Lewis and Brönstedt acids (cf. DE-A 1 543 178)  
10 and salts of nitrogen-containing bases and inorganic and/or organic acids (cf. DE-A 1 931 055).

Biuret-containing polyisocyanates are employed in particular in the paint industry as curing agents in coating systems whose  
15 binders generally comprise polymers having isocyanate-reactive groups.

So that the coating systems cure within a short period after application to a substrate to give coatings of good mechanical  
20 properties and high resistance to chemicals, it is necessary for the biuret-containing polyisocyanates to have a high content of NCO groups and a high level of reactivity with respect to the reactive groups in the binders.

In addition, the proportion of volatile isocyanates should be small even after prolonged storage, so as to enable safe  
25 processing of the biuret-containing polyisocyanates without the need for special safety precautions. So that these can be used to produce coating systems which exhibit good flow properties and a  
30 low solvent content, the paint industry demands products which at the same time are of low viscosity. Furthermore, the inherent color of the products should be minimal.

The biuret-containing polyisocyanates prepared by the known  
35 processes from tertiary alcohols and isocyanates, however, leave much to be desired, since they are too dark in color for many applications and, in particular after prolonged storage, still include considerable quantities of readily volatile monomeric isocyanates.

40 It is the object of the invention to provide an economic process by whose use it is possible to prepare biuret-containing polyisocyanates which are pale in color and whose content of volatile isocyanates, in particular after prolonged storage, is  
45 low.

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We have found that this object is achieved by a process for the preparation of polyisocyanates which contain one or more biuret groups, by reacting

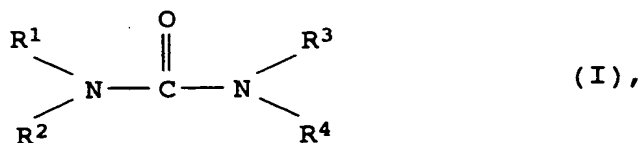
- 5 a) an aliphatic or cycloaliphatic isocyanate containing two or more isocyanate groups (isocyanate a) with
- b) a tertiary alcohol or a mixture of water and a tertiary alcohol (biuretizing agent b)

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at from 100 to 250°C, which comprises carrying out the reaction in the presence

- c) of a stabilizer (c) which constitutes a catalytic amount of urea, ammonia, biuret, a urea derivative of the formula I

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in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are hydrogen, C<sub>1</sub> to C<sub>10</sub> alkyl or C<sub>5</sub> to C<sub>10</sub> aryl, or

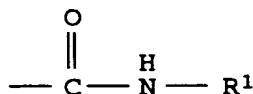
- 25 a carboxamide of the formula II



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in which R<sup>5</sup> is C<sub>1</sub> to C<sub>12</sub> alkyl which is unsubstituted or in which 1, 2 or 3 hydrogen atoms are replaced by a radical

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### DETAILED DESCRIPTION OF THE INVENTION

- Among the starting materials for the process of the invention,
- 40 suitable isocyanates (a) are polyfunctional isocyanates, especially aliphatic and cycloaliphatic di- and triisocyanates containing 4 to 30 carbon atoms. Particular examples are diisocyanates X(NCO)<sub>2</sub> in which X is an aliphatic hydrocarbon radical of 4 to 12 carbon atoms or a cycloaliphatic hydrocarbon
- 45 radical of 6 to 15 carbon atoms. Of particular significance in this respect are the commercially available starting compounds which are prepared industrially by the phosgenization of diamines

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by the process as described, for example, in DE-C 20 05 309 and DE-A 2 404 773 and by the phosgene-free process (biurethane cleavage) described in EP-B-0 126 299 (US-A-4 596 678), EP-B-0 126 300 (US-A-4 596 679), EP-A-0 355 443 (US-A-5 087 739) 5 and EP-A-0 568 782.

These are, in particular, 1,6-diisocyanatohexane (HDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (IPDI) and bis(4-isocyanatocyclohexyl)methane.

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Starting compounds which are of less importance in practice but of equal suitability in principle are isocyanates comprising 3 or more isocyanate groups, for example those which in addition include allophanate or isocyanurate groups. Examples of these are

15 the corresponding derivatives of HDI which are prepared by trimerization of HDI (cf. Kunststoff-Handbuch, volume 7, pp. 94 to 96, 3rd edition, 1993, Carl Hanser Verlag).

Particularly suitable biuretizing agents (b) are the tertiary 20 alcohols specified in DE-A 1 543 178, ie. especially monohydric alcohols of 4 to 20 carbon atoms, examples being 2-methyl-2-butanol, 2-methyl-2-pentanol, 3-methyl-3-pentanol, 3-ethyl-3-pentanol, 3-ethyl-3-nonanol, 3-methyl-1-butyn-3-ol, 3-methyl-1-pentyn-3-ol, 3,5-dimethyl-1-hexyn-3-ol, 25 1-methylcyclopentanol, 1-methylcyclohexanol, 1-ethylcyclohexanol, 1,1-diphenylethanol, 1,1,2-triphenylethanol and, in particular, tert-butyl alcohol. Mixtures of these alcohols are of course also suitable.

30 In addition to the tertiary alcohols, water in the form of an aqueous solution with the tertiary alcohols can also be used to biuretize the isocyanates (a). In this context, particularly suitable solutions of tertiary alcohol and water are those containing up to 80 mol%, preferably up to 40 mol%, of water, 35 based on the sum of the components of the mixture, since at these mixing ratios water is incorporated homogeneously and no oligomeric or polymeric urea derivatives, which precipitate from the reaction mixture, are formed in the course of the reaction with the isocyanates (a).

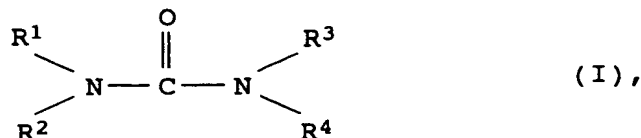
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In accordance with the invention, the isocyanate (a) is reacted with the biuretizing agent (b) in the presence of catalytic amounts of a stabilizer (c).

45 Suitable stabilizers (c) are urea, ammonia, biuret, a urea derivative of the formula I

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in which  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  and  $\text{R}^4$  are hydrogen,  $\text{C}_1$  to  $\text{C}_{10}$  alkyl, preferably methyl or ethyl, or  $\text{C}_5$  to  $\text{C}_{10}$  aryl, preferably phenyl or benzyl, or

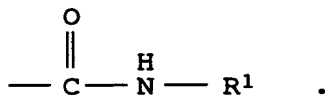
10 a carboxamide of the formula II



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in which  $\text{R}^5$  is a  $\text{C}_1$  to  $\text{C}_{12}$  alkyl, preferably  $\text{C}_1$  to  $\text{C}_6$  alkyl, which is unsubstituted or in which 1, 2 or 3 hydrogen atoms are replaced by a radical

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Examples of suitable urea derivatives are N-methylurea,  
25 N,N-dimethylurea, N,N'-dimethylurea, N-ethylurea,  
N,N-diethylurea, N,N'-diethylurea, ethyleneurea and N-phenylurea.

Suitable carboxamides of the formula II are formamide,  
N-methylformamide, acetamide, malonamide and succinamide.

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The stabilizers (c) are preferably employed in quantities of from 0.01 to 2.0 mol%, and with particular preference in quantities of from 0.05 to 1 mol%, based on the isocyanate groups in (a).

35 Using the process of the invention, the biuret-containing polyisocyanate can be prepared either continuously or batchwise.

A suitable apparatus for continuous preparation is, for example, a reactor cascade comprising a plurality of individual reactors

40 through which there is a continuous flow.

Batchwise preparation can be carried out, for example, in a stirred reactor.

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Normally, the isocyanate (a) is taken as initial charge and the biuretizing agent (b), in which the stabilizer (c) is advantageously already dissolved, is metered in.

- 5 The reaction is preferably carried out in bulk, although to reduce the viscosity it is also possible to use a solvent which is inert to isocyanate groups. Suitable solvents are those mentioned in DE-A 1 543 178, dioxane, tetrahydrofuran, triethylene glycol diacetate, toluene, benzene, chlorobenzene, 10 o-dichlorobenzene, butyl acetate, ethylene glycol monoethyl ether acetate and methylene chloride.

- In general the reaction is carried out under atmospheric pressure, although higher pressures of 1 to 10 bar are advisable, 15 for example, when using solvents or isocyanates (a) which boil below the preferred reaction temperatures.

- At the preferred temperatures, the reaction times are in general from 2 to 5 h. The reaction time is advantageously chosen such 20 that the theoretical NCO value is reached at the end. The theoretical NCO value is that NCO value possessed by the reaction mixture if the entire quantity of biuretizing agent employed has formed the quantity of biuret groups which are to be expected from theory.

- 25 As is known, the result of reacting an isocyanate group with a molecule of water or tertiary alcohol is an amino group which reacts with two further isocyanate groups to form a biuret group. Since the starting compounds employed include polyfunctional 30 isocyanates, the growth of the biuret-containing polyisocyanates therefore takes place in accordance with the kinetics of crosslinking reactions (cf. B. Vollmert, Grundriß der Makromolekularen Chemie, volume II, pp. 247 to 260, Vollmert-Verlag, Karlsruhe, 1988), with each biuret group forming 35 a branching point. In order to avoid the formation of relatively large branched-chain associations with two or more branching points, or even the occurrence of gelling, it is generally advisable to employ from 0.5 to 20 mol%, preferably from 2 to 10 mol%, of biuretizing agent, based on the isocyanate groups in 40 (a).

- Under these conditions, the isocyanates (a) react with the biuretizing agents predominantly to form mixtures of biuret-containing polyisocyanates whose principal component 45 comprises those biuret-containing polyisocyanates which are

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composed of three units derived from the isocyanate (a),  
containing only one biuret group.

Otherwise, it is possible by simple prior experimentation or  
5 calculation to determine the stoichiometric ratios at which  
mixtures of biuret-containing polyisocyanates are formed which  
have the desired average degree of polymerization.

In general, in order to obtain products which do not release  
10 hazardous quantities of isocyanates during processing, it is  
necessary to separate off the majority of the unreacted  
isocyanates (a) from the biuret-containing polyisocyanates  
formed. The usual desire is for products whose content of  
monomeric isocyanates (a) is less than 1% by weight, preferably  
15 less than 0.5% by weight, based on said biuret-containing  
polyisocyanates. The separation of the isocyanates (a) is  
advantageously carried out under reduced pressure at between 50°C  
and the chosen reaction temperature, for example by distilling  
off these isocyanates.

20 In the paint industry, the desire is in particular for  
biuret-containing polyisocyanates which are substantially free of  
solvents and from the isocyanates (a) used as starting materials,  
and which have a viscosity of from 2000 to 15,000 mPa·s,  
25 preferably from 2500 to 10,000 mPa·s (measured at a temperature of  
23°C and a shear gradient of 100 s<sup>-1</sup>).

Products with these viscosities are in general obtained when the  
stoichiometry of the starting products, the isocyanates (a) and  
30 the biuretizing agents (b), is chosen in accordance with the  
recommendation.

The products obtained by this process are distinguished in  
particular in that they couple comparatively low viscosity and a  
35 low content of volatile isocyanates of low molecular weight, like  
the isocyanates (a) used as starting materials, with a high NCO  
content and a high reactivity with respect to the binders  
employed in coatings, said binders containing isocyanate-reactive  
groups and being, for example, hydroxyl-containing polyacrylates.  
40 Particular advantages are that the content of volatile  
isocyanates does not rise even on prolonged storage of the  
products, and that the products are substantially colorless.

The products obtained by the process of the invention are  
45 particularly suitable as curing agents in the paint industry. The  
processing of these curing agents to give coating formulations,

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and the coatings produced therefrom, are items of general knowledge.

#### Examples

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General preparation procedure for the biuret-containing polyisocyanates (a)

504 g (3 mol) of 1,6-hexamethylene diisocyanate (HDI) are charged  
10 under nitrogen blanketing to a 1 l stirred reactor, and are  
heated to the reaction temperature indicated in the tables below.  
Then 14 mol%, based on the HDI, of biuretizing agent (b) and,  
dissolved therein, 0.2 mol%, based on the HDI, of the stabilizer  
(c) or of the acidic catalyst are added over the course of 2 min  
15 and the reaction mixture is stirred for 3 h. The reaction mixture  
is then distilled on a thin-film evaporator at 165°C and 2.5 mbar.

Departing from the above indications, the quantity of urea  
employed was

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0.4 mol% in Example 11,  
0.6 mol% in Example 12, and  
1.0 mol% in Example 13,

25 based in each case on the quantity of HDI.

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Table 1

Ex.	Biuretizing agent (b)	Stabilizer (c)	Temp. [°C]	NCO content [% by wt.]	Viscosity [mPa·s]	C N [Hazen]	Monomer content 0 d [% by wt.]	Monomer content 21 d [% by wt.]
1	tert-Butanol (tBuOH)	UR	180	22.0	4350	5	0.15	0.25
2	tBuOH	Eth UR	180	22.7	2290	10	0.20	0.41
3	tBuOH:water 19:1	UR	170	22.4	3340	7	0.08	0.22
4	tBuOH:water 19:1	UR	190	22.0	6030	10	0.10	0.21
5	tBuOH:water 19:1	Eth UR	180	22.7	2200	12	0.15	0.45
6	tBuOH:water 19:1	DM UR	180	22.7	2280	15	0.13	0.43
7	tBuOH:water 4.6:1	UR	180	22.2	5550	5	0.11	0.23
8	tBuOH:water 1.8:1	UR	180	22.0	6480	2	0.13	0.28
9	tBuOH:water 1:1	UR	180	22.2	5450	4	0.14	0.31
10	tBuOH:water 0.27:1	UR	180	21.4	12,600	10	0.14	0.28
11	tBuOH:water 1:1	UR	180	22.0	6120	12	0.12	0.27
12	tBuOH:water 1:1	UR	180	21.3	11,560	18	0.12	0.29
13	tBuOH:water 1:1	UR	180	20.8	18,200	22	0.13	0.25
14	tBuOH:water 19:1	Biuret	180	22.0	3860	15	0.14	0.27
15	tBuOH:water 19:1	Acetamide	180	22.6	3020		0.17	0.31
16	tBuOH:water 19:1	Samid	180	22.5	3000		0.14	0.34
17	tBuOH:water 19:1	Ammonia	180	22.0	2340	28	0.21	0.50

Table 2

Comp. Ex.	Biuretizing agent (b)	Acidic catalysts	Temp. [°C]	NCO content [% by wt.]	Viscosity [mPa·s]	C N [Hazen]	Monomer content 0 d [% by wt.]	Monomer content 21 d [% by wt.]
1	tert-Butanol (tBuOH)	BF <sub>3</sub>	150	22.9	2550	206	0.09	0.69
2	tBuOH	PTSS	150	21.7	5400	350	0.05	0.48
3	tBuOH	DEHP	180	22.0	4840	42	0.07	0.42
4	tBuOH	EHA	180	22.0	4660	38	0.09	0.42
5	tBuOH	HAc	180	22.1	4330	55	0.08	0.40
6	tBuOH	-	180	22.9	2130	44	0.09	0.53
7	tBuOH:water 19:1	PTSS	180	22.0	5550	371	0.11	0.91
8	tBuOH:water 19:1	PTSS	150	21.8	5360	256	0.03	0.49
9	tBuOH:water 19:1	DEHP	180	22.4	3800	32	0.10	0.53
10	tBuOH:water 19:1	EHA	180	22.4	3650	10	0.15	0.63
11	tBuOH:water 19:1	ClAc	180	22.3	3970	56	0.14	0.53
12	tBuOH:water 19:1	-	180	22.7	2090	32	0.12	0.61

## Notes on Tables 1 and 2

## Compounds employed

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The biuretizing agents employed were tert-butanol (tBuOH) and mixtures thereof with water. The figures given thereafter indicate the molar ratio of the components in the mixture

- 10 UR = urea  
EthUR = ethyleneurea  
DM UR = N,N'-dimethylurea  
BF<sub>3</sub> = boron trifluoride as the dihydrate  
PTSA = p-toluenesulfonic acid  
15 DEHP = di(2-ethylhexyl) phosphate  
EHA = 2-ethylhexanoic acid  
HAc = acetic acid  
Samid = succinamide  
ClAc = chloroacetic acid  
20 Ammonia = ammonia in the form of a 25% strength by weight aqueous solution

## NCO content:

- The NCO content is given in % by weight and was measured in  
25 accordance with DIN 53 185.

## Viscosity:

The viscosity data relate to measurements made at 23°C with a shear gradient of 100 s<sup>-1</sup>.

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## Color number (CN):

The color number was determined in accordance with DIN ISO 6271 and is indicated in Hazen scale units.

35 Monomer content:

The monomer content indicates the quantity of monomeric isocyanate in % by weight present in the respective biuret-containing polyisocyanate directly after preparation (0 d) or after storage for 21 days at 50°C (21 d). It was measured in

- 40 accordance with DIN 55 956.

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